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14. ABSTRACT
Extensive research on mixed metal oxide nanomaterials to serve as destructive adsorbents and photocatalysts for detoxifying chemical warfare agents, toxic industrial chemicals, and biotoxins was carried out. This involved advanced inorganic synthesis, characterization, and testing (and test methodology development). Aerogel and xerogel synthetic methods to high surface area titanium oxide, silicon oxide, and mixed TiO2-SiO2 were used. Metal ions of chromium, vanadium, manganese, iron, cobalt, nickel, and silver were added to enhanced

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Report Title

Oxidation Catalysts in the Dark and the Light--Final Report

ABSTRACT

Extensive research on mixed metal oxide nanomaterials to serve as destructive adsorbents and photocatalysts for detoxifying chemical warfare agents, toxic industrial chemicals, and biotoxins was carried out. This involved advanced inorganic synthesis, characterization, and testing (and test methodology development). Aerogel and xerogel synthetic methods to high surface area titanium oxide, silicon oxide, and mixed TiO2-SiO2 were used. Metal ions of chromium, vanadium, manganese, iron, cobalt, nickel, and silver were added to enhanced photochromic properties, in particular, for visible light wavelengths. Structural characterization employed many methods: electron microscopy, x-ray diffraction, electron spin resonance, infrared and ultraviolet spectra, elemental analyses, and more. Testing involved specialized photochemical methodology, gas-chromatography-mass spectrometry, numerous chemical and biological agents or surrogates. Considerable progress was made toward the discovery of universal solid decontamination materials. Especially high surface area TiO2 with added silver, chromium, vanadium, manganese, carbon, and/or sulfur (selected transition metal ions and selected non-metals) are very promising. Also, some evidence as to how these photocatalysts function was gained.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

1. Ranjit, Koodali T.; Klabunde, Kenneth J.; "Catalysis by Metal Oxides," Surface and Nanomolecular Catalysis, ed. Ryan Richards, CRC Press, NY, Ch. 2, pgs. 40-61, 2006.
2. Ranjit, Koodali T.; Martyanov, Igor N.; Demydov, Dmytro; Uma, Sitharaman; Rodrigues, Shalini; Klabunde, Kenneth J.; "A Review of the Chemical Manipulation of Nanomaterials using Solvents:Gelation Dependent Structures," J. Sol-Gel Sci. Technol. 40, 335-339 (2006).
3. Jeevadandam, P.; Klabunde, K.J.; "Adsorbents," Chapter 14, (invited book chapter), Synthesis, Properties, and Applications of Oxide Nanomaterials, Wiley, Hoboken, NJ, Rodriguez, A., Fernandez,-Garcia, M., editors, John Wiley and Sons, 2007.
4. Koper, O.B.; Rajagopalan, S.; Winecki, S.; Klabunde, K.J.; Chapter 1, pgs. 3-25 (invited book chapter), "Nanoparticle Metal Oxides for Chlorocarbon and Organophosphonate Remediation," Environmental Applications of Nanomaterials, ed. G. Fryxell, Imperial College Press, London, and World Scientific Publishing, Singapore (2007).
5. Kakkar, R.; Kapoor, P.N.; Klabunde, K.J.; "First Principles Density Functional Study of the Adsorption and Dissociation of Carbonyl Compounds on Magnesium Oxide Nanostructures," J. Phys. Chem. B. 110, 25941-25949 (2007).
6. Hamal, D.; Klabunde, K.J.; "Synthesis, Characterization, and Visible Light Activity of New Nanoparticle Photocatalysts Based on Silver, Carbon, and Sulfur Doped TiO2," J. Colloid Int. Sci., 311, 514-522 (2007).
7. Yang, X; Cao, C.; Hohn, K.; Erickson, L.; Maghirang, R.; Hamal, D.; Klabunde, K.; "Highly Visible-Light Active C-, V-Doped TiO2 for Oxidation of Acetaldehyde," J. Catalysis, 252, 296-302 (2007).
8. Beavers, E.; Cabazes, H.; Grassian, V.; Gutowski, T.; Hutchinson, J.; Klabunde, K.J.; Larsen, S.; Mansoori, A.; Russell, A.; Shah, S.I.; Velegol, D.; Zhang, W.; "Nanotechnology Applications for Sustainable Manufacturing Processes," in Nanotechnology and the Environment (Report of a National Nanotechnology Initiative Workshop held May 8-9, 2003, Arlington, VA); organizers, Karn, B.; Roco, M.; Masciangioli, T.; Savage, N.; National Science and Technology Council Committee on Technology, Chap. 4, pgs. 21-24 (2007).
9. Singh, M.; Zhou, N.; Paul, D.K.; Klabunde, K.J.; "IR Spectra Evidence of Aldol Condensation: Acetaldehyde Adsorption over TiO2 Surface," J. Catalysis, 260, 371-379 (2008).
10. Yang, X.X.; Cao, C.; Erickson, L.; Hohn, K.; Maghirang, R.; Klabunde, K.; "Synthesis of Visible-Light-Active TiO2 Based Photocatalysts by Carbon and Nitrogen Doping," J. Catalysis 260, 128-133 (2008).
11. Häggström, J.A.; Stoimenov, P.K.; Klabunde, K.J.; "Synthesis and Characterization of Nanosized Halogenated and Interhalogenated Metal Oxide Adducts," Chem. Materials 20, 3174-3183 (2008).
12. Smetana, A.; Klabunde, K.J.; Marchin, G.R.; Sorensen, C.M.; "Biocidal Activity of Nanocrystalline Silver Powders and Particles," Langmuir 24, 7457-7464 (2008).
13. Chang, C.A.; Ray, B.; Paul, D.K.; Demydov, D.; Klabunde, K.J.; "Photocatalytic Reaction of Acetaldehyde over SrTiO3 Nanoparticles," J. Molec. Catal. A: Chemical, 281, 99-106 (2008).
14. Yang, X.; Cao, C.; Erickson, L.; Hohn, K.; Maghirang, R.; Klabunde, K.; "Photo-Catalytic Degradation of Rhodamine B on C-, S-, N-, and Fe-Doped TiO2 under Visible Light Irradiation," Appl. Catal. B.: Environmental, 91, 657-662 (2009).
15. Hamal, D.B.; Kalebaila, K.K.; Klabunde, K.J.; "Mixed-Metal Oxide Nanomaterials for Environmental Remediation," in Nanomaterials for the Life Sciences, Vol. 3; Mixed Metal Nanomaterials, Kumar, C.S.S.R., editor; Ch. 5, pgs. 139-161, Wiley-VCH, Weinheim (2009).
16. Klabunde, K.J.; Richards, R.M.; Nanoscale Materials in Chemistry, Second Edition, Wiley, New York (2009). Also, two chapters written for this book: Martyanov, I.N.; Klabunde, K.J.; "Photocatalytic Purification of Water and Air over Nanoparticulate TiO2," Ch. 17, pgs. 581-604; Pickrell, J.A.; Erickson, L.E.; Dhakal, K.; Klabunde, K.J.; "Toxicity of Inhaled Nanomaterials," Ch. 22, pgs. 729-769.

Number of Papers published in peer-reviewed journals: 16.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

Four presentations at contractor meetings and professional meetings

Number of Presentations: 4.00

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Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Hamal, D.; Häggström, J.; Marchin, G.; Ikenberry, M.; Hohn, K; Klabunde, K.J.; "A Multifunctional Biocide/Sporocide and Photocatalyst Based on Titanium Dioxide (TiO2) Co-Doped with Silver, Carbon, and Sulfur," Langmuir, in press. DOI:10.1021/la9002844r

Number of Manuscripts: 1.00

Number of Inventions:

Graduate Students

NAME	PERCENT_SUPPORTED
Dambar Hamal	0.50
Xiangxin Yang	0.50
Manindu Peiris	0.25
Johanna Haggstrom	0.50
Dmytro Demydov	0.50
FTE Equivalent:	**2.25**
Total Number:	**5**

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Kennedy Kalebaila	0.25
P. Jeevanandam	0.25
FTE Equivalent:	**0.50**
Total Number:	**2**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Kenneth Klabunde	0.05	No
FTE Equivalent:	**0.05**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Xiangxin Yang
Johanna Haggstrom
Dmytro Demydov
Dambar Hamal
Total Number: **4**

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)